

On the analytical solutions of the Hamiltonian of a Frenkel exciton for the lattice of a regular polyhedral cluster

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The Coulomb Hamiltonian of a small-radius exciton on a cluster whose atoms occupy the sites of a group lattice is studied. The spectrum of Frenkel excitons can be obtained analytically for definite modes by the methods of harmonic analysis of the lattice Hamiltonian. The carbon cluster C_{60} with icosahedral symmetry is given as an example.

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This letter presents a method for calculating the spectrum of small-radius excitons (Frenkel excitons¹) in atomic clusters whose atoms occupy the sites of a two-dimensional group lattice. The importance of this problem is due to, on the one hand, the latest progress made in the synthesis of different nonmetallic clusters of carbon, silicon, nitrides, and other materials and, on the other hand, the fact that the investigation of the physical properties of these quantum objects requires a theory going beyond the single-electron approximation. Different theoretical estimates made primarily in the Hubbard model, and also various experimental data obtained for the intensively investigated cluster C_{60} , attest to the need to take into account the Coulomb interaction between the electrons of a cluster. The adequate incorporation of this interaction is still an unsolved problem.

Quantum-size effects are manifested in most nonmetallic clusters in that an energy gap exists between the occupied and unoccupied discrete cluster levels and optically allowed transitions occur with excitation of an electron–hole pair, possessing a dipole moment, through the gap. An important manifestation of the Coulomb interaction of the carriers is renormalization of the frequency of such a transition as a result of the binding of carriers into an exciton. We note that the structure of the clusters is such that the carrier motion on a closed curved surface is quasi-two-dimensional.² Depending on the ratio of the kinetic energy of the carriers and the Coulomb interaction energy, different theoretical models are used to describe an exciton. If an electron–hole pair is strongly localized on a lattice site (i.e., its kinetic energy is low), a Frenkel exciton is formed,³ in contrast the more common situation occurring in bulk semiconductor materials, where the Coulomb interaction is strongly weakened by dielectric screening and a large-radius exciton arises⁴ (Wannier–Mott exciton). In clusters the kinetic energy of the carriers can

be low because of the low two-dimensional electron density on the surface of the cluster, while the Coulomb energy is fixed, since the distance between the carriers does not exceed the size of the cluster. Thus, the condition for the existence of a *small-radius exciton* can be satisfied. In the present letter we present a method for diagonalizing the Hamiltonian of a Frenkel exciton on a group lattice of various structure of clusters of semiconductor materials. As already mentioned, experimental data exist for fullerene C_{60} , so that this icosahedral carbon cluster will be studied as an illustrative example (see, also Refs. 5 and 6). The final group lattice is defined as a lattice each of whose sites can be obtained from an initial site by a definite rotation from a point group given beforehand.⁷ It is natural to assign to the initial site the group identity element e . In the case of C_{60} these rotations carry a truncated icosahedron into itself (details can be found in Refs. 4–6). All sites of the group lattice are equivalent and possess z bonds with nearest neighbors. The number z is determined by the number of group elements formed.

We shall proceed from the condition that the electrons are strongly localized on sites, so that an atom in an excited state remains neutral. We assume the excitation energy to be small compared with the atomic energy. This makes it possible to study transitions only between the nearest levels. We are interested primarily in an optical transition associated with a change in the parity of the electron wave function, specifically, $s \rightarrow p$. The Coulomb interaction of excited atoms is determined in the first nonvanishing order³ by the dipole–dipole term (we recall that excitation preserves the electrical neutrality of the atom):

$$V = \frac{1}{2} \sum'_{g, g'} \frac{1}{r^3(g, g')} [\mathbf{P}_g \cdot \mathbf{P}_{g'} - 3(\mathbf{P}_g \cdot \mathbf{e}(g, g'))(\mathbf{P}_{g'} \cdot \mathbf{e}(g, g'))], \quad (1)$$

where \mathbf{P}_g and $\mathbf{P}_{g'}$ are the dipole moments of the sites g and g' ; $\mathbf{r}(g, g')$ is the distance between the sites; $\mathbf{e}(g, g') = \mathbf{r}(g, g')/|\mathbf{r}(g, g')|$; and, the prime on the sum means that the summation extends over $g \neq g'$. In the second-quantized representation the energy can be written in terms of the creation and annihilation operators of dipole excitations on the sites. One should remember that in our case of an excitation from a level s to a level p the electron wave function has three components, while the wave function of the electron–hole excitation, having three mutually perpendicular polarization directions, is a polar vector. As a result of this, the components of the excitation creation and annihilation operators have the form $\mathbf{p}_i^\dagger(g) = a_i^\dagger(g)d^\dagger(g)$, where $a_i^\dagger(g)$ and $d^\dagger(g)$ are electron and hole creation operators at the site g . The Coulomb part of the Hamiltonian operator has the form

$$\hat{V} = \frac{1}{2} \sum'_{g, g'} \frac{1}{r^3(g, g')} \mathbf{p}^\dagger(g) \cdot \hat{\tau}(g, g') \cdot \mathbf{p}(g'), \quad (2)$$

where the angular part of the dipole–dipole interaction operator, $\hat{\tau}(g, g')$, depends only on the directions to interacting atoms located at the sites g and g' , and it does not depend on the distance between the sites and can be represented by a traceless antisymmetric tensor of rank 2:

$$\tau(g, g')_{ij} = \delta_{ij} - 3\mathbf{e}(g, g')_i \mathbf{e}(g, g')_j, \quad (3)$$

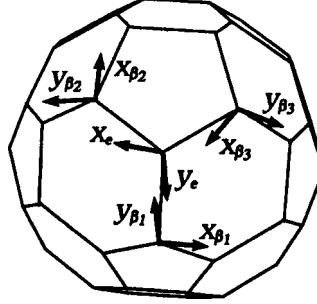


FIG. 1. Diagram showing the construction of local coordinate systems for a C_{60} cluster. The local axes $x(g)$ and $y(g)$ are shown for the base site $g=e$ and three nearest neighbors $g'=\beta_i$. The z axes at each site are directed in a radial direction.

where δ_{ij} is the Kronecker delta. The distance dependence of expression (2) is separated into the cofactor $r^{-3}(g, g')$.

We have already assumed the excitation to be strongly localized. Therefore it is natural to take account of the interaction of nearest neighbors only. It is convenient to characterize the neighboring sites of a chosen site by corresponding rotations from the group of the lattice. We denote the neighbors of the site g as βg , where β is one of z group operators. It follows from the group properties that this set is identical for all sites (in the case of C_{60} there are three rotations $\{C_5, C_5^{-1}, C_2\}$).⁸ To investigate the sum (2) it is convenient to switch from the laboratory coordinate system tied to the basis site e defined above to local coordinate systems (LCSs) tied to an arbitrary site. This will make it possible to simplify the expression by separating in the operator τ the part that is invariant under the group rotations. For the specific example of the lattice of the icosahedral C_{60} cluster it is convenient to introduce the LCS as follows⁹ (see Fig. 1): Orient the z axis from the site radially away from the cluster; orient the y axis in a plane passing through the z axis and an edge connecting two hexagons; and, define the x axis by the product $\mathbf{y} \times \mathbf{z}$. For this choice the transition from the LCS at the site g of the cluster to the LCS at the site g' is evidently given by the rotation $\hat{D}^{(T)}(g'g^{-1})$, which transfers the first site into the second site. We denote the rotation of the laboratory coordinate system in the LCS at the site g as $\hat{D}^{(T)}(g^{-1})$. Then the operator creating a dipole at the site g , given in the LCS tied to it, is given by $\mathbf{p}_{g_i}^\dagger = D_{ij}^{(T)}(g^{-1})\mathbf{p}_j^\dagger(g)$.

The Coulomb part of the Hamiltonian in the LCS acquires the form (we temporarily drop the indices corresponding to the polarization of the excitation)

$$V = \frac{1}{2} \sum_{g, \beta} \frac{1}{r_\beta^3} \mathbf{p}_g^\dagger [\hat{D}^{(T)}(g^{-1})]^\dagger \hat{\tau}(g, \beta g) \hat{D}^{(T)}([\beta g]^{-1}) \mathbf{p}_{\beta g} = \frac{1}{2} \sum_{g, \beta} \frac{1}{r_\beta^3} \mathbf{p}_g^\dagger \hat{\tau}_\beta \mathbf{p}_{\beta g}. \quad (4)$$

For generality we retain the difference in the bond lengths, r_β , for the nearest neighbors. One can see that the operator $\hat{\tau}_\beta$ depends only on the rotation β fixing the pair of neighbors, and it does not depend on the specific position of a pair of sites in the cluster. Therefore expression (4) can be put into the maximally compact form by a harmonic expansion over a group (see below).

The components of the matrix τ_β in explicit form are:

$$\begin{aligned}\tau_{\beta ij} &= [D^{(T)}(\beta^{-1}) - 3(D^{(T)}(g)\mathbf{e}_{g,\beta_g}) \otimes (D^{(T)}(\beta g)\mathbf{e}_{g,\beta_g})]_{ij} \\ &= D^{(T)}(\beta^{-1})_{ij} - 3 \frac{(D^{(T)}(e)_{i3} - D^{(T)}(\beta^{-1})_{i3})(D^{(T)}(\beta^{-1})_{3j} - D^{(T)}(e)_{3j})}{|D^{(T)}(e)_{i3} - D^{(T)}(\beta^{-1})_{i3}|^2},\end{aligned}\quad (5)$$

where $D^{(T)}(e)$ denotes the identity rotation. To find the eigenstates of the Hamiltonian (4) it is necessary to solve a secular equation of order $3N$, where N is the number of atoms in the cluster (for C_{60} , of the order of $3 \times 60 = 180$), which makes it difficult to obtain an analytical solution.

We now use the symmetry properties of the Hamiltonian and switch in Eq. (4) from a sum over lattice sites to a sum over irreducible representations (IRs) of this group. For this we expand the components of the dipole excitation creation operator $\mathbf{p}_{g_i}^\dagger$ over all IRs contained in the regular representation of the group. In what follows, unless indicated explicitly, summation over repeated indices is assumed:

$$\mathbf{p}_i^\dagger(g) = a_i^\dagger(g) d^\dagger(g) = D_{n_1 m_1}^{*(\alpha_1)}(g) a_{i; n_1 m_1}^{\dagger(\alpha_1)} D_{n_2 m_2}^{*(\alpha_2)}(g) d_{n_2 m_2}^{\dagger(\alpha_2)}, \quad (6)$$

where $D_{ij}^{(\alpha)}(g)$ are the Wigner matrices for the IR α and the group element g , and the creation operators on the right-hand side of the equation create an electron (hole) in the symmetry state of the IR α . Switching to the coupled basis for the electron-hole excitation creation operator and transforming the product of Wigner matrices, we obtain

$$\mathbf{p}_i^\dagger(g) = C_{n_1 m_1, n_2 m_2, k_1, k_2}^{\alpha_1, \alpha_2, \gamma} a_{i; n_1 m_1}^{\dagger(\alpha_1)} d_{n_2 m_2}^{\dagger(\alpha_2)} D_{k_1 k_2}^{*(\gamma)}(g) = D_{k_1 k_2}^{*(\gamma)}(g) \mathbf{p}_{i; k_1 k_2}^{\dagger(\gamma)}, \quad (7)$$

where $\mathbf{p}_{i; k_1 k_2}^{\dagger(\gamma)}$ is by definition the creation operator of an exciton in the IR γ , while $C_{n_1 m_1, n_2 m_2, k_1, k_2}^{\alpha, \beta, \gamma}$ are the Clebsch-Gordan coefficients for intercoupling the corresponding representations.¹⁰ Substituting the excitonic creation and annihilation operators (7) into the Coulomb Hamiltonian (4), expanding the rotation operator $\hat{D}^{(\gamma)}(\beta g)$ into a product of the corresponding rotation operators for β and g , and summing over the group lattice using the orthogonality relations for unitary transformations, we obtain the final form of the Coulomb Hamiltonian

$$H_0 + V = H_0 + \frac{1}{2} \sum_{\beta} \frac{1}{r_{\beta}^3} \sum_{\gamma} \mathbf{p}_{i; k, n}^{\dagger(\gamma)} \tau_{\beta ij} D_{mk}^{(\gamma)}(\beta) \mathbf{p}_{j; m, n}^{(\gamma)}. \quad (8)$$

One can see that the dipole interaction matrix in this expression is a direct product of the operator $\hat{\tau}_{\beta}$, which depends only on the group element β fixing the pair of interacting dipoles, and the rotation matrix of this element, given in one of the IRs. Thus, instead of a secular equation of dimension $3N$ we now need to solve a set of identical equations with the dimensions $3n$, where n is the dimension of the corresponding IR, i.e., 3, 9, 12, and 15 for C_{60} . This made it possible to find analytical solutions for some modes of the system.^{5,6} An important feature of our method is the possibility of performing a symmetry analysis of the desired two-particle excitations, since the form of the corresponding IR determines uniquely the possibility of constructing a nonzero matrix element between this excited state and the ground (completely symmetric) state of a cluster for any exci-

tation potential. This makes it possible to solve the problem only for the modes of interest to us, for example, for the five dipole-active modes T_{1u} in the case of C_{60} (Ref. 5).

We have presented a method for systematically calculating the spectrum of the Coulomb Hamiltonian given on the lattice of a regular polyhedral cluster, the symmetry group of whose lattice makes it possible to use the method of harmonic analysis of the matrix of the Coulomb interaction and switch from the initial coordinate representation to the space of irreducible representations of the given group lattice. Diagonalization of the Hamiltonian, obtained in the Frenkel exciton approximation, in the space of electron-hole excitations makes it possible to classify the states by symmetry and also gives the spectrum and wave functions of the two-particle modes of a system where the Coulomb energy is much greater than the kinetic energy of the carriers.

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